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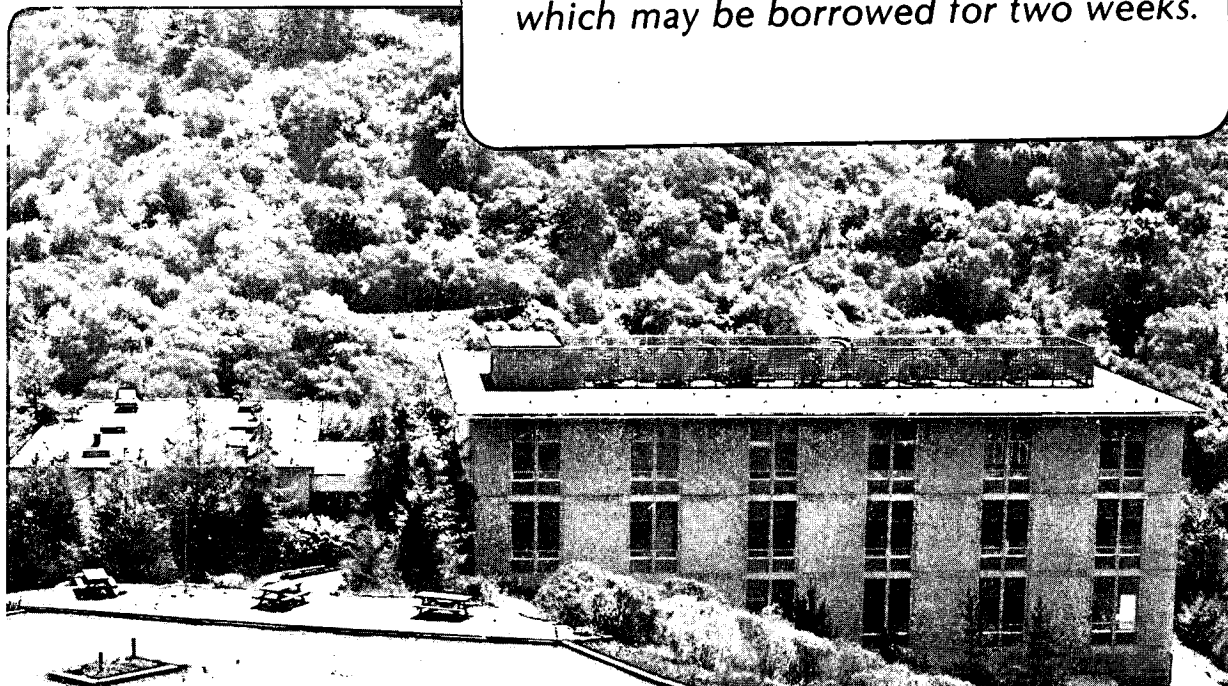
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Photodissociation of Vinyl Bromide and
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Photodissociation of Vinyl Bromide

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Abstract.

We have performed measurements of the translational energy distributions and anisotropy parameters of the photodissociation products of vinyl bromide at 193 nm. Br-atom and HBr elimination were observed with a branching ratio between the two channels of $1.28 \pm .05$. Both processes occurred with a large release of translational energy, an average of about 2.0 eV for the Br-atom channel and somewhat less for HBr elimination. The maximum release of translational energy for Br + C_2H_3 formation led to an upper limit of 77 ± 3 kcal/mol to $D_o(C_2H_3-Br)$, from which an upper limit to the heat of formation of the vinyl radical, 71 ± 3 kcal/mol, was derived. This result was used to reexamine crossed molecular beams data relevant to the determination of the vinyl radical heat of formation. A metastable state of C_2H_3 observed in the photodissociation of vinyl bromide was interpreted as the formation of $C_2H_3(\tilde{A}^2A'')$.

Introduction.

While it is true that the precise nature of the potential energy surface (PES) determines the dynamics and rate of a reaction, in the absence of such information the determination of reliable thermochemical data for molecular radicals is one area that promises to shed a great deal of light on their chemical behavior.[1] Moreover, a quantitative misunderstanding of thermochemistry can lead to completely incorrect conclusions concerning the rate of a reaction, especially for near thermoneutral ones. This is graphically illustrated by the exothermic reaction of vinyl radical with molecular oxygen

$$C_2H_3 \;+\; O_2 \;\longrightarrow\; C_2H_2 \;+\; HO_2$$
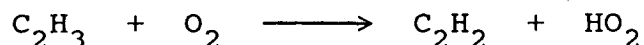
which until recently was thought to be considerably endothermic and therefore unimportant.[2]

The heat of formation of the vinyl radical is particularly important, not only because it is related to the C-H bond energy of ethylene, but also because the exact energy required to eliminate a highly reactive H-atom from the vinyl radical producing C_2H_2 will have a major impact on the complex combustion chemistry of small hydrocarbons. The suggested values for the heat of formation of the vinyl radical have ranged over ~13 kcal/mol due to problems mentioned below.[3] In spite of these difficulties, most recent experimental and theoretical determinations are now converging on a value of 107 ± 3 kcal/mol. The experimental results which will be described

in this paper are also in agreement with this range.

Traditionally, thermochemical data for radicals have been obtained from the determination of activation energies of reactions involving the radical of interest, for example bond fission or atom abstraction reactions. However, due to the complexities of bulk experiments and the blossoming of wavelength-dependent photoionization mass spectrometry, the heats of formation of many radicals have been obtained from the threshold energies for various ionization processes. A good example is the determination of the heat of formation of the C_2H radical by finding the dissociative photoionization threshold of $C_2H_2 \longrightarrow C_2H^+ + H + e^-$,[4] and combining this with the ionization potential (IP) of C_2H.[5]

While the <u>precision</u> of such measurements is typically high, ~1 kcal/mol, there are a number of possible <u>systematic</u> difficulties associated with threshold determinations that can give rise to large deviations between experiments. First, the photoionization cross-section near threshold is very small and often difficult to identify. Second, it must be assumed that ion formation is <u>possible</u> at the thermodynamic threshold.[6] In addition, ordinarily only positive ions are detected. For dissociative photoionization, there is the possibility of an ion-pair production channel that can form the positive ion of interest slightly below the true dissociative ionization threshold.[7] Finally, the thermochemical cycles used in these determinations can be very complex. Each leg of a cycle is an

opportunity for the accumulation of error, and the refinement
or redetermination of a previously well accepted thermochemical
quantity can have a ripple effect on many different experi-
ments.[8]

The method of photofragmentation translational spectros-
copy has been shown to yield accurate thermochemical data for
molecular radicals. By photodissociating a molecule at wave-
lengths substantially above the dissociation threshold where
the absorption cross-section is large, and measuring the
maximum release of translational energy, E_T^{MAX}, of the products,
the bond energy of the parent molecule can often be determined
in a very direct manner, avoiding many of the problems just
mentioned.[9] For example, a determination of the heat of
formation of C_2H was made recently using this method to find
the C-H bond energy in C_2H_2 as shown below.[9]

$$C_2H_2 \xrightarrow{\text{193.3 nm}} C_2H + H + E_T \qquad D_0(C_2H\text{-}H) = E_{photon} - E_T^{MAX}$$
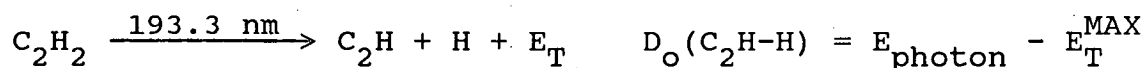
In addition to obtaining heats of formation for ground state
radicals, electronically excited radicals may also be formed in
UV photodissociation, and by doing high resolution translation-
al energy measurements, these states can be resolved and
studied.[10]

The purpose of this paper is to present results obtained
on the UV photodissociation of C_2H_3Br which, in addition to
illuminating many characteristics of the UV photochemistry of
C_2H_3Br, provide an upper bound on the heat of formation of

C_2H_3. In addition, a metastable state of C_2H_3, containing enough energy to dissociate to C_2H_2 + H but with a dissociation lifetime longer than 100 μsec. was observed in the photodissociation experiment. The possible identity of this state and the implications of the photodissociation results will also be discussed.

Experimental.

The photodissociation experiments were performed on a molecular beam apparatus which has been described elsewhere.[9] The instrument consists of three parts: a rotating molecular beam source, a fixed, ultra-high vacuum, mass-spectrometric detector, and a "main" interaction chamber linking the two. A continuous molecular beam was formed by passing 150 torr of a 10% mixture of vinyl bromide in helium through a .125 mm nozzle heated to 280°C to prevent cluster formation. The vinyl bromide beam had a peak velocity of 6.9 x 10^4 cm/sec. The beam was skimmed and a region of differential pumping separated the source region and the main chamber. A pulsed laser beam, propagating along the rotation axis of the beam source, crossed the molecular beam, creating a pulse of dissociation products.

A small angular fraction of this pulse of products travelled through two regions of differential pumping, and was then ionized in a liquid nitrogen cooled detector chamber by a Brink-type electron-impact ionizer, 36.75 cm from the molecular/laser beam crossing point. Ions produced were
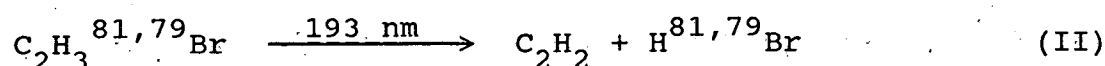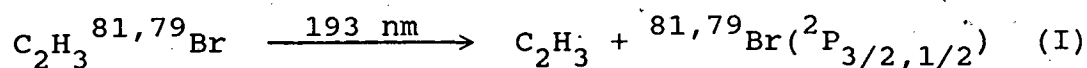
directed through a quadrupole mass filter, then to an ion counter. Time-of-flight (TOF) spectra of the dissociation products were recorded on a 256 channel scaler with a minimum channel width of 1 μsec. which was triggered by the laser pulse. Data acquisition was directed by a DEC LSI-11 computer.

In order to reduce background due to molecules which originate in the main chamber, bounce off a surface in the line-of-sight of the detector, then pass directly through all the apertures of the detector and are therefore unaffected by differential pumping, a closed cycle helium refrigerator was used to cool a copper plate directly behind the interaction region in the viewing region of the detector to 30 K. Liquid nitrogen was also supplied to the main chamber to cool large copper panels serving as additional cryopumps for vinyl bromide.

Most of the experiments were performed using the light from an unpolarized ArF laser, emitting at 193.3 nm (Lambda-Physik EMG 103 MSC). Typically, 100 mJ/pulse at 150 Hz were obtained and focused to a 1 mm x 3 mm rectangular spot. In order to obtain information on the vinyl bromide excited state lifetime, the laser was polarized with a MgF_2 prism. The center-of-mass (c.m.) frame relative translational energy distributions of the products, $P(E_T)$, were derived from the observed laboratory frame TOF spectra using a forward convolution method.[9]

Results.

1. Photodissociation Using an Unpolarized Laser.- TOF spectra were obtained for mass-to-charge ratio's (m/e's) of 26, 27, 79, 80, 81, and 82. The two important dissociation channels are reactions I and II.

$$C_2H_3{}^{81,79}Br \xrightarrow{\text{193 nm}} C_2H_3 + {}^{81,79}Br({}^2P_{3/2,1/2}) \quad \text{(I)}$$

$$C_2H_3{}^{81,79}Br \xrightarrow{\text{193 nm}} C_2H_2 + H^{81,79}Br \quad \text{(II)}$$

The m/e = 27 TOF spectrum, measured at an angle of 90° from the molecular beam, is shown in fig. 1 and is due solely to vinyl radicals produced in reaction I. Fig. 2 is an energy level diagram for reactions I and II, from which it is clear that even in the event of formation of spin-orbit excited $Br({}^2P_{1/2})$, unless at least 25 kcal/mol of energy goes into translation there will be sufficient energy for C_2H_3, produced in reaction I, to decompose into C_2H_2 + H as shown in reaction III.

$$C_2H_3Br \longrightarrow C_2H_3 + Br({}^2P_{1/2}) \longrightarrow C_2H_2 + H + Br({}^2P_{1/2}) \quad \text{(III)}$$
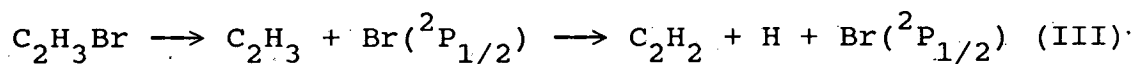
This is predicted simply on the basis of the known heats of formation of atoms and molecules.[11] A careful inspection of fig. 1 reveals a pronounced change in the slope of the data between 29 and 27 kcal/mol translational energy release. In addition, the existence of substantial signal below 25 kcal/mol of translational energy implies the existence of some meta-stable state of C_2H_3.

In the absence of secondary decomposition, the TOF

spectrum of either C_2H_3 or Br would by itself be sufficient to give the $P(E_T)$ for reaction I, since linear momentum must be conserved. In reality, because some vibrationally excited C_2H_3 can decompose, it is necessary to obtain the Br-atom TOF spectrum in order to derive the $P(E_T)$. For this, we must first determine the contribution of $H^{81}Br$ from reaction II that appears as m/e = 81 signal due to fragmentation in the electron-impact ionizer. By analyzing the m/e = 82 TOF spectrum, due to $H^{81}Br^+$ as shown in fig. 3a, we can account for the long slow tail in the m/e = 81 TOF spectrum, shown as the dot-dashed curve in fig. 3b. The remaining portion of the m/e = 81 TOF spectrum is due solely to Br-atom formation.

The $P(E_T)$ for production of Br-atoms in reaction I (dashed curve) along with the $P(E_T)$ for production of vinyl radicals (solid curve) is shown in fig. 4. The $P(E_T)$'s are identical on the fast side of the distribution, where C_2H_3 is formed with low internal energies, but below a translational energy of about 40 kcal/mol the $P(E_T)$ for vinyl formation drops below that for Br-atom formation due to secondary decomposition of C_2H_3. At translational energies below about 20 kcal/mol the $P(E_T)$'s converge again, indicating the presence of the metastable component in the data. By subtracting the solid curve from the dashed curve in fig. 4, the reaction I $P(E_T)$ for the subset of vinyl radicals which decompose is obtained (see fig. 5).

As mentioned previously, if only $Br(^2P_{1/2})$ were formed, we

would expect C_2H_3 molecules with kinetic energies as low as 25 kcal/mol to survive. Because the molecular beam is heated, some vibrational energy in the C_2H_3Br could end up in the vinyl radical after C_2H_3Br dissociation and cause it to decompose further even if as much as 30 kcal/mol appears in translation. The secondary loss of vinyl radicals produced with as much as 40 kcal/mol of translational energy is unambiguous evidence that $Br(^2P_{3/2})$ is also produced in reaction I, where an extra 10.5 kcal/mol of spin-orbit excitation energy becomes available.

The most direct observation of secondary decomposition is the m/e = 26 TOF spectrum taken at 90° from the molecular beam, shown in fig. 6. There are three components to this TOF spectrum, two of which are determined from other data. These are: (1) vinyl radical also observed at m/e = 27, (2) C_2H_2 (acetylene or vinylidene) from reaction II which is derived from the m/e = 82 data based on linear momentum conservation, and (3) acetylene from spontaneous secondary decomposition of vibrationally hot vinyl radical.

The analysis of secondary decomposition in molecular beam experiments has been described elsewhere.[9] In short, there are two $P(E_T)$'s used to generate curve (3). The first is shown in fig. 5 and is used to calculate the primary lab frame velocity vector distribution of the vinyl radicals which undergo secondary decomposition. The second $P(E_T)$ is the translational energy release of the secondary process, reaction IV.

$$C_2H_3^{\ddagger} \longrightarrow C_2H_2 + H \qquad\qquad (IV)$$

Here the double-dagger indicates substantial vibrational excitation. Because Br is three times heavier than C_2H_3 and there is a large translational energy release for reaction I, the recoil velocity of the vinyl radical is very large. In comparison, reaction IV releases very little energy and the loss of a light H-atom changes the original velocity of the vinyl radicals so little that the TOF spectrum of C_2H_2 from reaction IV, curve (3) in fig. 6, is only dependent on the "difference $P(E_T)$" derived from fig. 4 and shown in fig. 5. The fit to the m/e = 26 data, curve (3) of fig. 6, was generated directly from this $P(E_T)$ and as such is a good second check on the two $P(E_T)$'s shown in fig. 4.

2. Photodissociation Using Polarized Light.- The general form of the c.m. product angular distribution for photodissociation with linearly polarized light, $I(\theta) \sim 1 + \beta P_2(\cos\theta)$, has been derived by Zare.[12] β is an anisotropy parameter that ranges between 2 (a $\cos^2\theta$ distribution about the laser polarization vector, $\underline{\epsilon}$) and -1 (a $\sin^2\theta$ distribution) and θ is the angle between $\underline{\epsilon}$ and the c.m. frame recoil velocity vector of the products. For the derivation of β, the vinyl radicals were detected at 90° from the beam and the change in the magnitude of the signal depending on whether $\underline{\epsilon}$ was parallel or perpendicular to the detection axis was measured.

It has been shown that measured angular distributions of photodissociation products are subject to saturation effects.[13]

Because the absorption cross-section is dependent on the orientation of the molecule with respect to $\underline{\epsilon}$, transitions of favorably oriented molecules can be saturated at lower laser powers than those of unfavorably oriented molecules. Fig. 7 shows the magnitude of the m/e = 27 signal as a function of laser power for $\underline{\epsilon}$ parallel and perpendicular to the detector direction. The ratio of the two is directly related to β. While the parallel signal is always larger than the perpendicular signal, the ratio varies above ~3 mJ/pulse, indicating that orientation-dependent saturation is indeed occurring. In the linear regime, however, the ratio is constant and a value for β of 0.45 ± 0.02 is derived for reaction I.

In contrast to vinyl radical formed in process I, the heavier HBr formed in process II is much slower. Simultaneously fitting both the shape and the relative magnitudes of the TOF spectra with $\underline{\epsilon}$ either parallel or perpendicular to the detector direction, a value of $\beta = 0.70 \pm 0.02$ for process II was obtained. Fig. 8 shows the two HBr TOF spectra and the fits to the data.

The magnitude of β depends on many factors, among which relaxation of the molecular configuration and rotation between excitation and decomposition are important. The fact that β is quite different for the two channels implies that either the two channels arise from different electronic transitions or the dynamics of the two channels after excitation are substantially different. The $P(E_T)$ for reaction I clearly shows that it is a

direct dissociation from the electronically excited state. On the other hand, reaction II might follow internal conversion to the ground state. The different β values could also mean that the average exit impact parameters for the two processes are quite different.

Knowing the amount of signal measured for each channel and the corresponding β and $P(E_T)$, the branching ratio between the two channels can be calculated.[14] The m/e = 81 TOF spectrum was used since it had contributions from both channels, which precludes any error from fluctuating beam intensities. The branching ratio between Br-atom and HBr formation was found to be 1.28 ± .05, corresponding to 55 ± 1% Br-atom production.

Discussion.

Fig. 2 shows clearly that the difference between the photon energy, E_{photon}, and the maximum release of translational energy for reaction I, E_T^{MAX}, is the C-Br bond energy in vinyl bromide, assuming that it is possible to form some products in their ground states. Fig. 1 shows that E_T^{MAX} is 71 ± 3 kcal/mol and since E_{photon} is 148 kcal/mol, an upper limit to the C-Br bond energy in vinyl bromide is 77 ± 3 kcal/mol.

Knowing the heats of formation of C_2H_3Br and $Br(^2P_{3/2})$,[11] one can derive a rigorous upper limit to the heat of formation of vinyl radical of 71 ± 3 kcal/mol, corresponding to an upper limit to the C-H bond energy in ethylene of 108 ± 3 kcal/mol. Here ± 3 kcal/mol reflects the uncertainty associated with the

measurement of E_T^{MAX}. The amount of error between this upper limit and the heat of formation of C_2H_3 rests upon the validity of the assumption that products can be formed in their lowest quantum states.

There are a number of ways that this assumption could be wrong. For example, if it were impossible to form Br in anything but the spin-orbit excited $^2P_{1/2}$ state, our determination of E_T^{MAX} would be too high by 10.5 kcal/mol, the spin-orbit splitting in Br. As shown earlier, however, we know that Br($^2P_{3/2}$) is indeed formed.

The most likely limit to the accuracy of the assumption of lowest quantum state product formation is due to product rotational excitation. When the C-Br bond breaks in reaction I, the repulsive energy release is mainly along the C-Br bond, and it is quite unlikely that the Br-atom departs along a trajectory with zero impact parameter. This and the large translational energy release can generate a substantial amount of orbital angular momentum between the C_2H_3 and Br pair and produce rotationally excited vinyl radical. The magnitude of this error is of critical importance. If products formed with the maximum translational energy still contained some rotational energy, the estimated C-H bond energy in ethylene should be lowered by that amount. In the light of an unambiguous upper limit to $D_0(C_2H_3-H)$ of 108 ± 3 kcal/mol, it is interesting to reevaluate other experiments with bearing on this problem.

In an infrared chemiluminescence experiment, Sloan et

al.[15] have shown that the highest HF vibrational level observable from the reaction $F + C_2H_4 \longrightarrow HF + C_2H_3$ was $v' = 3$, $J' = 3$. If 1.5 RT of collision energy contributed to the excitation of the products, their observation would yield an upper limit to the C-H bond energy in C_2H_4 of 104 kcal/mol. Of course, if the formation of this highest rovibrational state of HF, $v' = 3$, $J' = 3$, is accompanied by excitation of the internal degrees of freedom of C_2H_3 or kinetic energy release between HF and C_2H_3, the C-H bond energy in C_2H_4 will be lower by a corresponding amount. In an earlier crossed molecular beam study of $F + C_2D_4 \longrightarrow C_2D_3 + DF$ carried out in our laboratory,[16] a pronounced feature with forward-backward peaking and a relatively narrow angular distribution,[17] which corresponds to a relatively small translational energy release, was observed (see fig. 9). Because of the substantial exothermicity, if the products were formed in their ground states and carried away the excess energy in translational motion, the DF product would have been spread too wide and thin to be detected in that experiment. The relatively sharp DF feature is most likely to be DF formed in the highest energetically allowed vibrational state. If we assume the DF product to be in $v = 4$, since the maximum translational energy release, which limits the width of the laboratory angular distribution and corresponds to the formation of DF ($v = 4$, $J = 0$), is 1.3 kcal/mol, the upper limit to the C-D bond energy in C_2D_4 will have a value of 106 kcal/mol. Considering the difference in the zero point energies between

the dissociation processes of C_2D_4 and C_2H_4,[18] a C-D bond energy of 106 kcal/mol is exactly what is expected from the value of 104 kcal/mol in C_2H_4 and is consistent with the results of the C_2H_3Br experiment.

Of course, if DF were to be formed in v = 3 rather than v = 4, the C-H bond energy of 104 kcal/mol in C_2H_4 will have to be adjusted by 7.5 kcal/mol, the energy difference between DF (v = 4) and DF (v = 3),[19] which gives a value of 111.5 kcal/mol. This value is just at the edge of the experimental error of the upper limit determined in the C_2H_3Br experiment, but this assignment of the vibrational state is incompatible with the results of Sloan et al.[15]

Although there is strong evidence from three different experiments that $D_o(C_2H_3-H)$ is as low as 104 kcal/mol, and a clear upper limit of 111 kcal/mol has been found in this work, a series of recent studies on the C-H bond energy by various methods has still not fully converged. The threshold energy of H^+ formation from C_2H_4 in a photoionization study gave a value of 114 kcal/mol which,[20] however, is incompatible with the upper bound from the photodissociation experiment. Photodissociation of C_2H_3Br in this work, photoionization of C_2H_3,[21] electron detachment of $C_2H_3^-$,[22] and the reaction $Cl + C_2H_4 = C_2H_3 + HCl$[23] all gave values of around 108 kcal/mol. A value of 110 kcal/mol was calculated in a recent ab initio study.[24] On the other hand, from the maximum energy release in the reaction between $F + C_2H_4$ and C_2D_4, a value of 104 kcal/mol is

implied. If the assignment of the vibrational state of DF formed is correct, this should be the most accurate result. Summarizing all the data available, the true value should be 107 ± 3 kcal/mol. Due to the importance of this radical, further investigation is clearly required in the future.

As mentioned before, the slow tail on the m/e = 27 TOF spectrum, fig. 1, is due to metastable C_2H_3. It is clear that if the internal energy of the vinyl radicals were in the form of molecular vibration, unless the exit barrier for C_2H_3 dissociation is substantial,[25] there would be nothing to keep those with less than 25 kcal/mol of translational energy from decomposing. However, since the $\tilde{A}^2A''$ state does not correlate adiabatically with the ground electronic states of C_2H_2 + H, if the molecule were to be formed electronically excited, the decomposition rate could be very slow. Then the molecule might be able to survive long enough either to reach the detector or fluoresce. From the absorption cross-section,[26] the fluorescence lifetime is approximately 100 μsec. or less and could explain the observation of a metastable state if internal conversion were as slow as this.
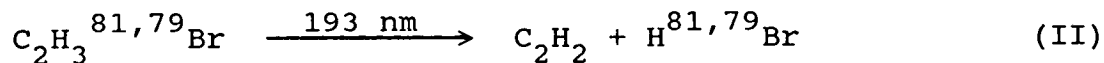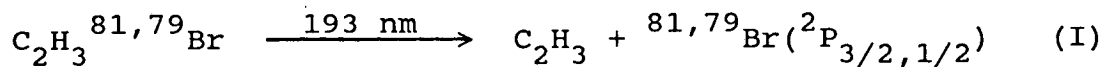
Based on this interpretation, the maximum release of translational energy for the formation of excited state vinyl radical is assigned to the point where the slope of the data begins to change noticeably, 29 ± 2 kcal/mol. The resulting heat of formation for C_2H_3 $\tilde{A}^2A''$ is 113 ± 2 kcal/mol. Combining this value with $\Delta H_f(C_2H_3)$ = 67 kcal/mol, consistent with the Cl

and crossed beam results discussed above, a $T_{oo}(\tilde{A} \leftarrow \tilde{X})$ in C_2H_3 of 46 ± 2 kcal/mol is obtained. If $\Delta H_f(C_2H_3)$ is closer to 71 kcal/mol, then $T_{oo}(\tilde{A} \leftarrow \tilde{X}) = 42 \pm 2$ kcal/mol results.

The absorption spectrum of the C_2H_3 radical near 500 nm has been observed and ab-initio calculations have verified the presence of an excited electronic state in this energy range.[26] The considerable change in geometry upon electronic excitation makes it difficult to observe the (0←0) transition in absorption, although a 1205 cm^{-1} progression was observed and attributed to the C-C stretch in the $\tilde{A}$ state. By extrapolating the progression, one obtains a predicted T_{oo} of 46.9 kcal/mol, assuming that the lowest observed transition at 20,020 cm^{-1} is from $v' = 3 \leftarrow v'' = 0$. If the lowest observed transition is however $v' = 4 \leftarrow v'' = 0$, $T_{oo} = 43.5$ kcal/mol. Both interpretations of the absorption data are energetically consistent with the derived ΔH_f for C_2H_3 in the $\tilde{A}$ state.

Conclusions.

In the photodissociation of C_2H_3Br, the important collision-free dissociation processes were found to be the following.

$$C_2H_3{}^{81,79}Br \xrightarrow{\quad 193 \text{ nm} \quad} C_2H_3 + {}^{81,79}Br(^2P_{3/2,1/2}) \qquad (I)$$

$$C_2H_3{}^{81,79}Br \xrightarrow{\quad 193 \text{ nm} \quad} C_2H_2 + H^{81,79}Br \qquad (II)$$

The Br-atom channel accounted for a little more than half of the total signal. By measuring E_T^{MAX} for the products of

process I, an upper limit to the heat of formation of C_2H_3 was found to be 71 ± 3 kcal/mol. This corresponds to an upper limit to the C-H bond energy in ethylene of 108 ± 3 kcal/mol and was used to help determine the highest energetically allowed DF product vibrational state in the reactive scattering experiment on F + $C_2D_4 \longrightarrow C_2D_3$ + DF(v').[16] This determination is in agreement with the chemiluminescence studies of F + $C_2H_4 \longrightarrow C_2H_3$ + HF(v',J') by Sloan et al.[15], and gives a value for the C-H bond energy of 104 kcal/mol.

A metastable state of C_2H_3 was also formed in the photo-dissociation of C_2H_3Br. This is probably due to electronically excited vinyl radical ($\tilde{A}^2A''$) which cannot decompose to ground state C_2H_2 + H within ~100 μsec.

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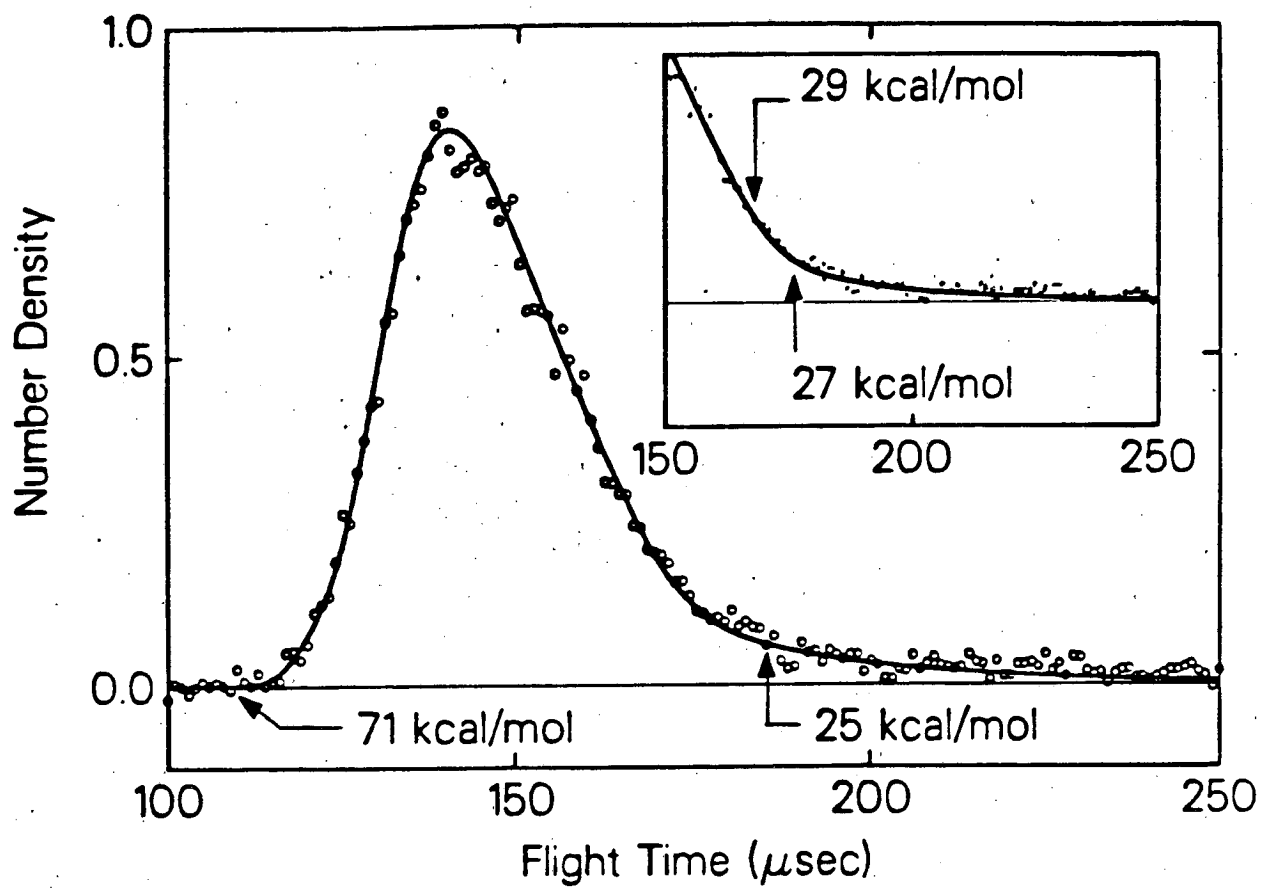
Figure Captions.

Fig. 1   TOF spectrum at m/e = 27, 90° from beam. Open
           circles are data and the solid line is the fit to the
           data based on the $P(E_T)$ shown as the solid curve in
           fig. 4. The insert shows a magnified view of the
           onset of metastable C_2H_3 (see text).

Fig. 2   Energy level diagram for the photodissociation of
           vinyl bromide. Energies are in kcal/mol.

Fig. 3   TOF spectra of the Br containing products. (a) m/e =
           82 at 30° from the molecular beam. (b) m/e = 81 at
           30° from the beam. Open circles are the data points.
           The solid lines are the fits to the data. In (b) the
           dot-dashed curve is due to HBr from reaction II and
           the dashed curve is due to Br-atoms from reaction I.

Fig. 4 $P(E_T)$'s for production of vinyl radical (solid curve)
           and Br-atoms (dashed curve).

Fig. 5 $P(E_T)$ for those vinyl radicals which undergo seconda-
           ry decomposition.

Fig. 6   TOF spectrum for m/e = 26 at 90°. Open circles are
           data. The solid line is the fit to the data based on
           three components: (1) vinyl radicals, dashed curve,
           (2) C_2H_2 from reaction II, dot-dashed curve, and (3)
           acetylene from the secondary decomposition of vibra-
           tionally hot vinyl radicals, triple dot-dashed curve.

Fig. 7 $m/e = 27$ signal intensity as a function of laser
          power for two laser polarization angles. The open
          circles correspond to parallel polarization while the
          closed circles correspond to perpendicular polariza-
          tion.

Fig. 8 $m/e = 82$ TOF spectra as a function of laser
          polarization. Open circles are data and the solid
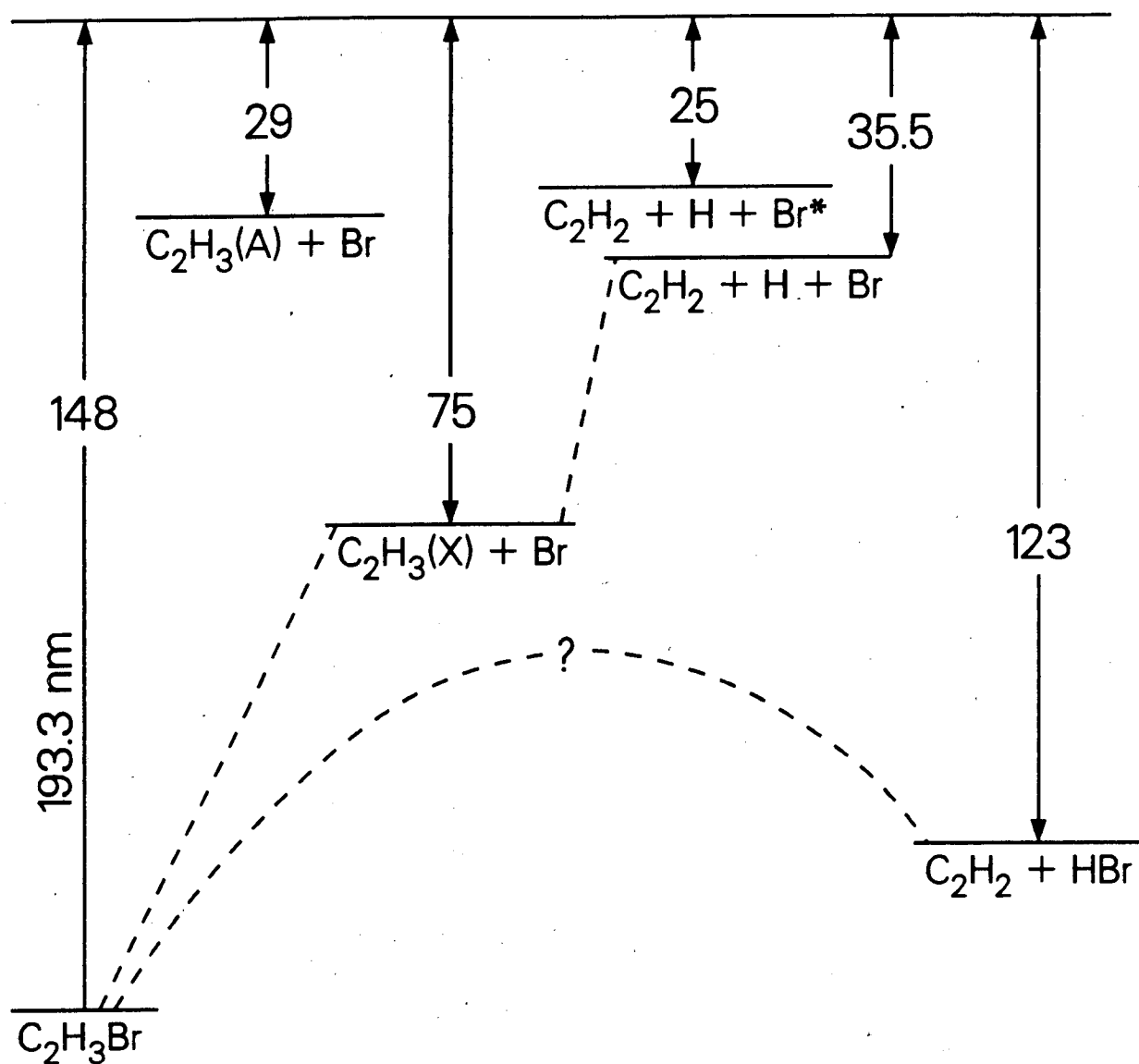   line is the fit to the data based on an anisotropy
          parameter of 0.70.

Fig. 9   Angular distribution of the DF product from the
          reaction of $F + C_2D_4 \longrightarrow C_2D_3 + DF(v = 4)$. The
          circles are the data points. The solid line shows
          the best fit to the data based on the $P(E_T)$ in fig.
          10. Offsetting the $P(E_T)$ by ± 0.5 kcal/mol gives the
          other two curves.

Fig. 10 $P(E_T)$ for the reaction products in fig. 9.

Fig. 1

Fig. 2

XBL 8811-3908

Fig. 3

XBL 8610-3669

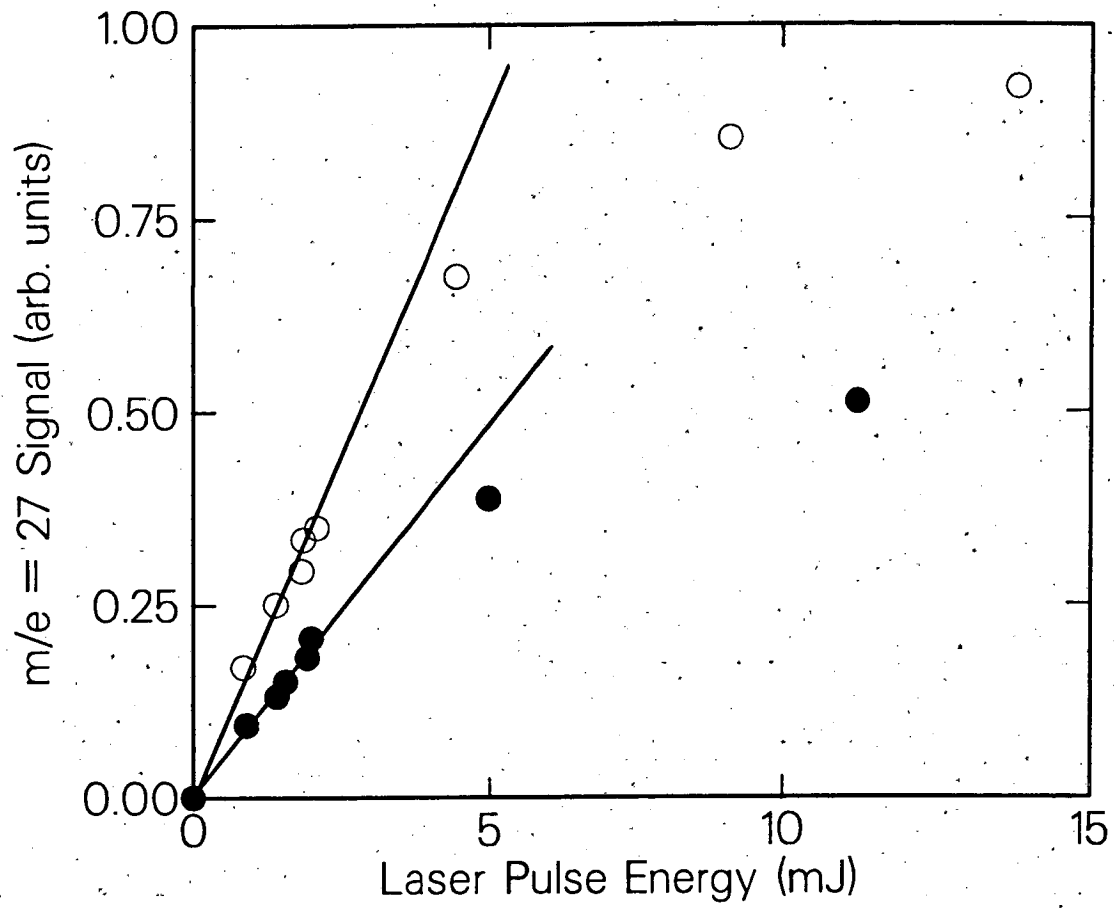Translational Energy Release (kcal/mol)
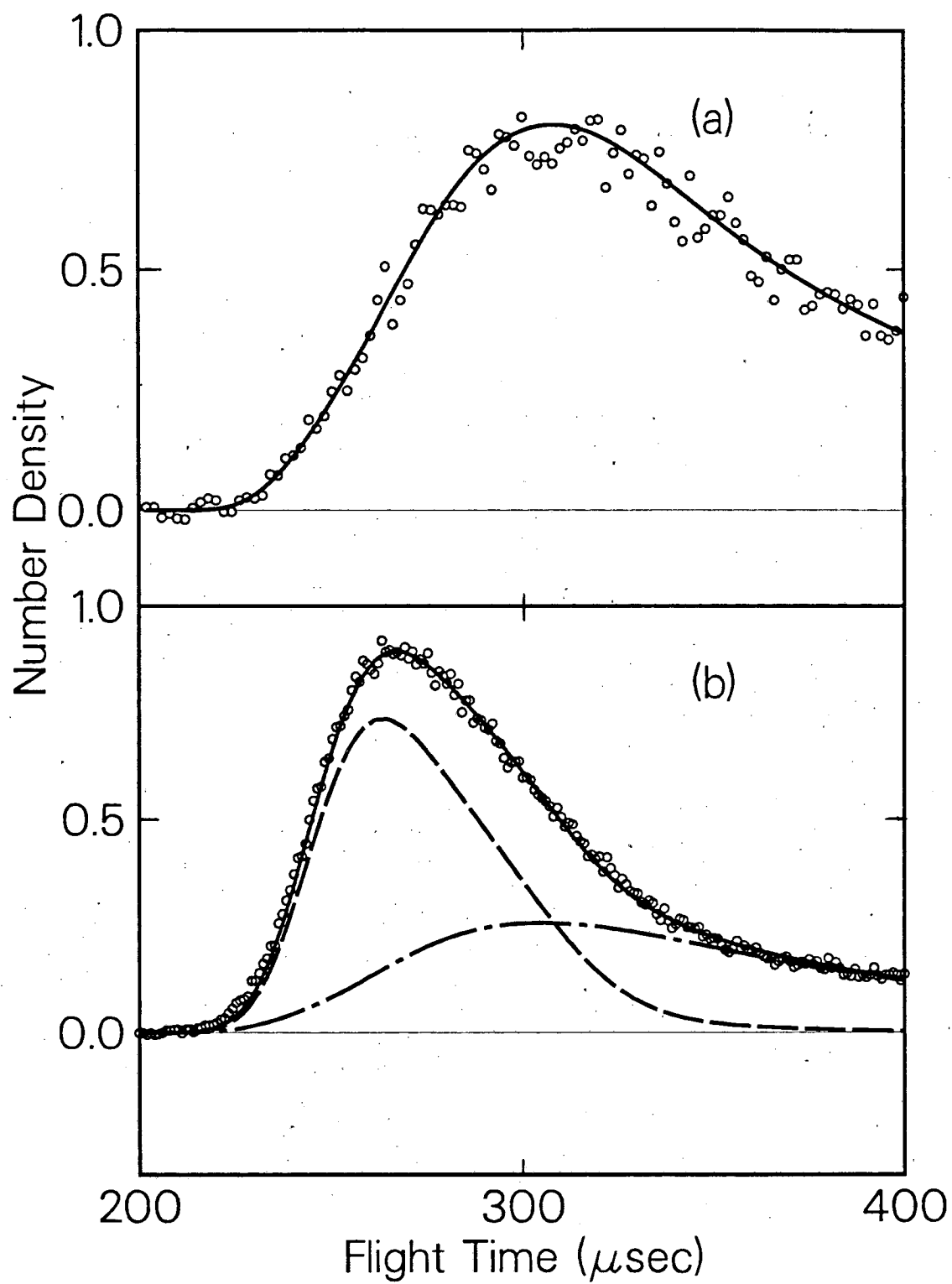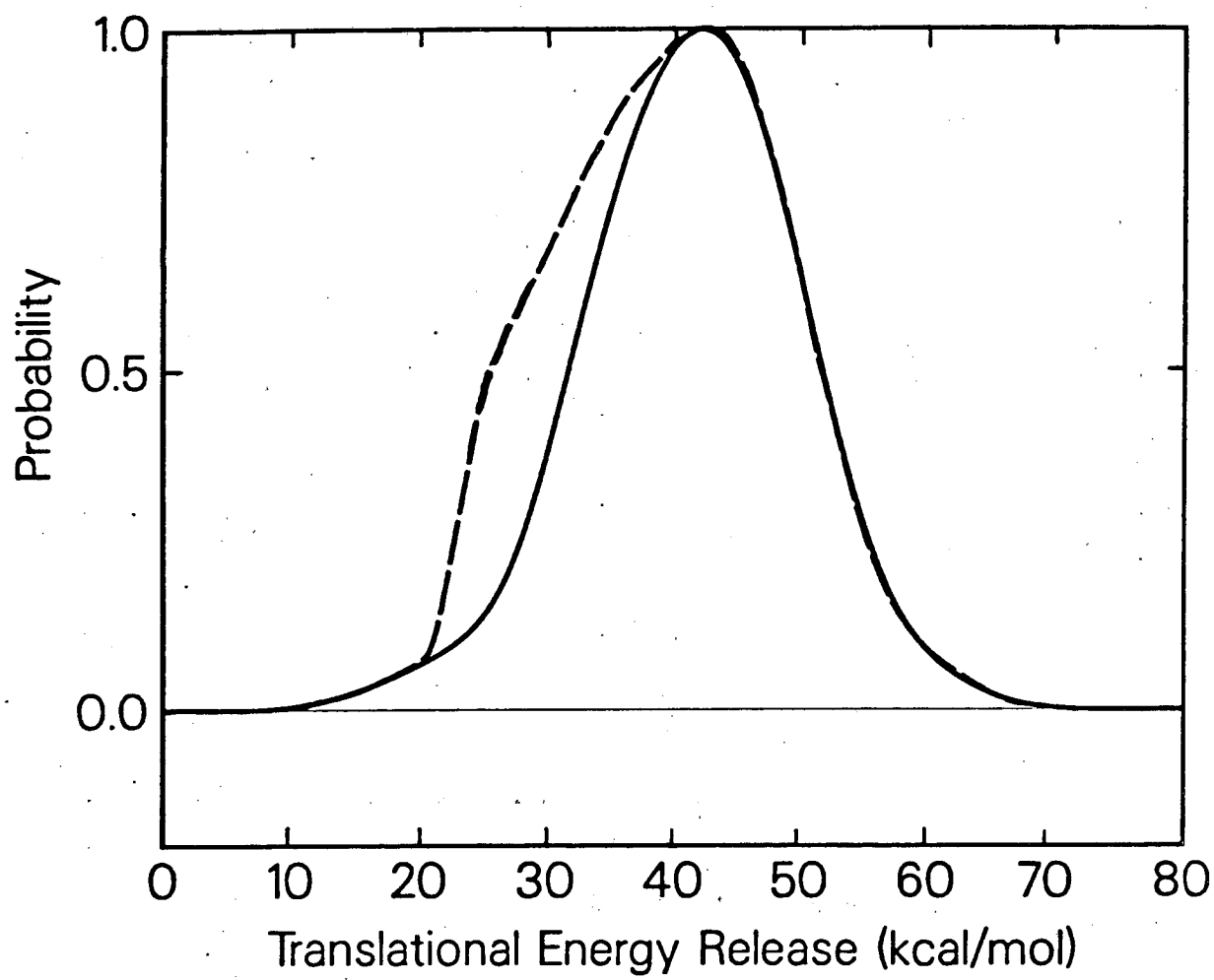
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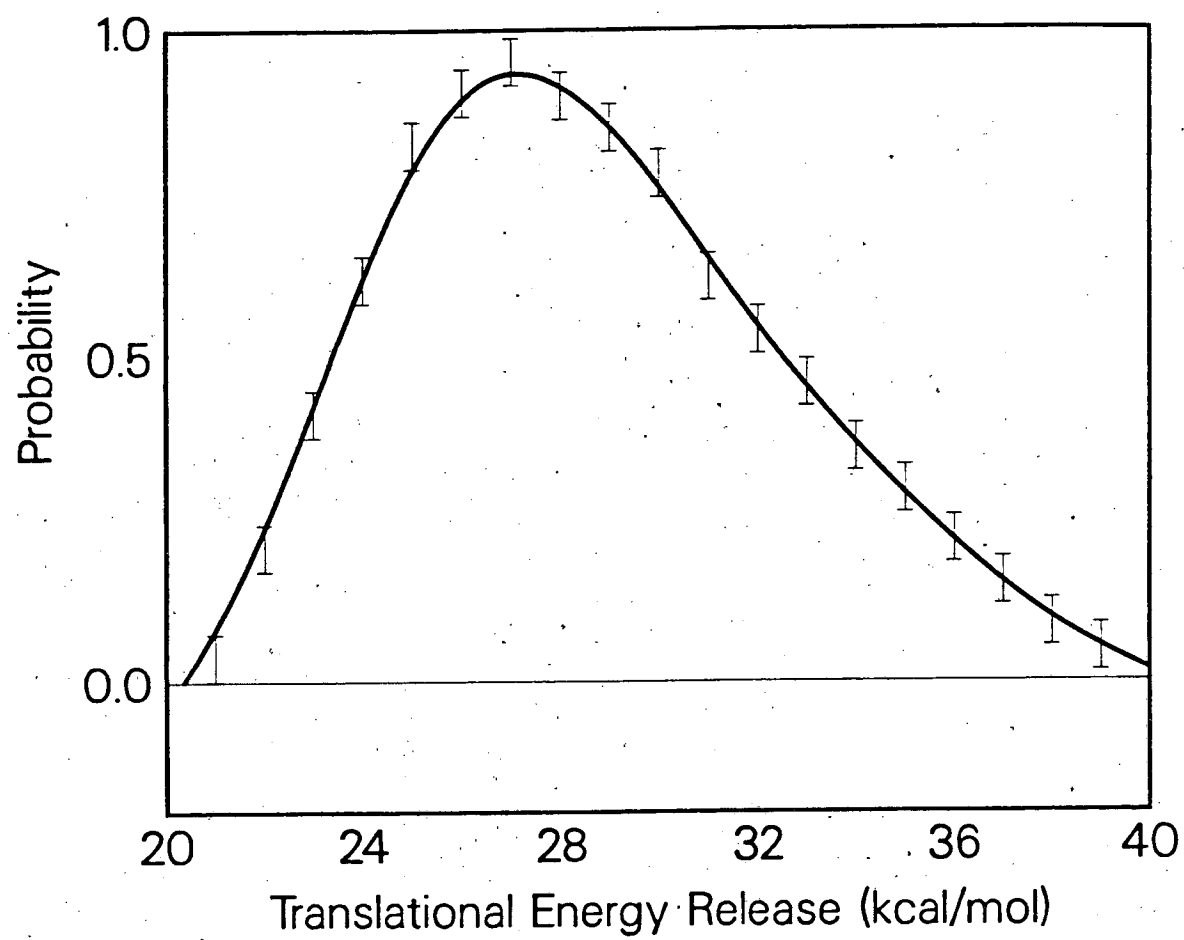
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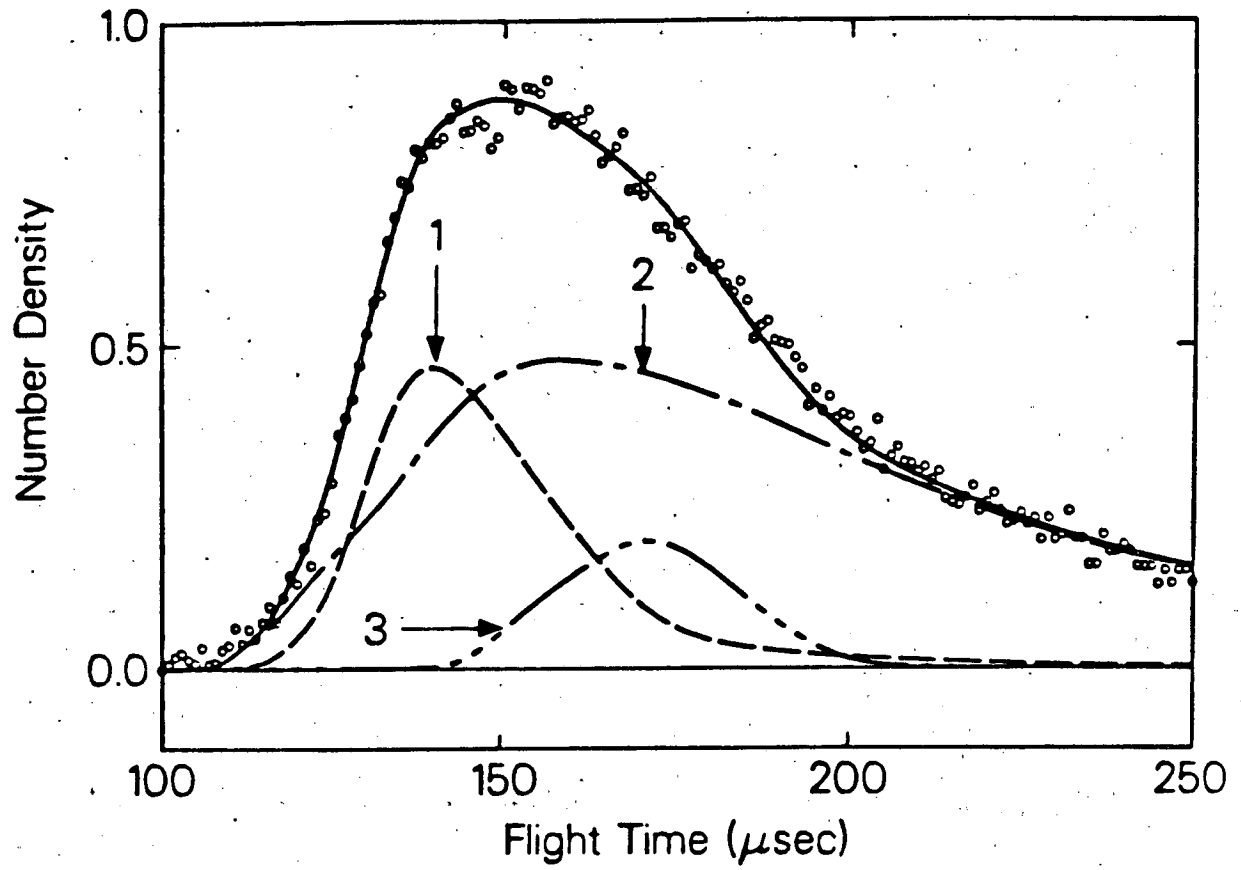
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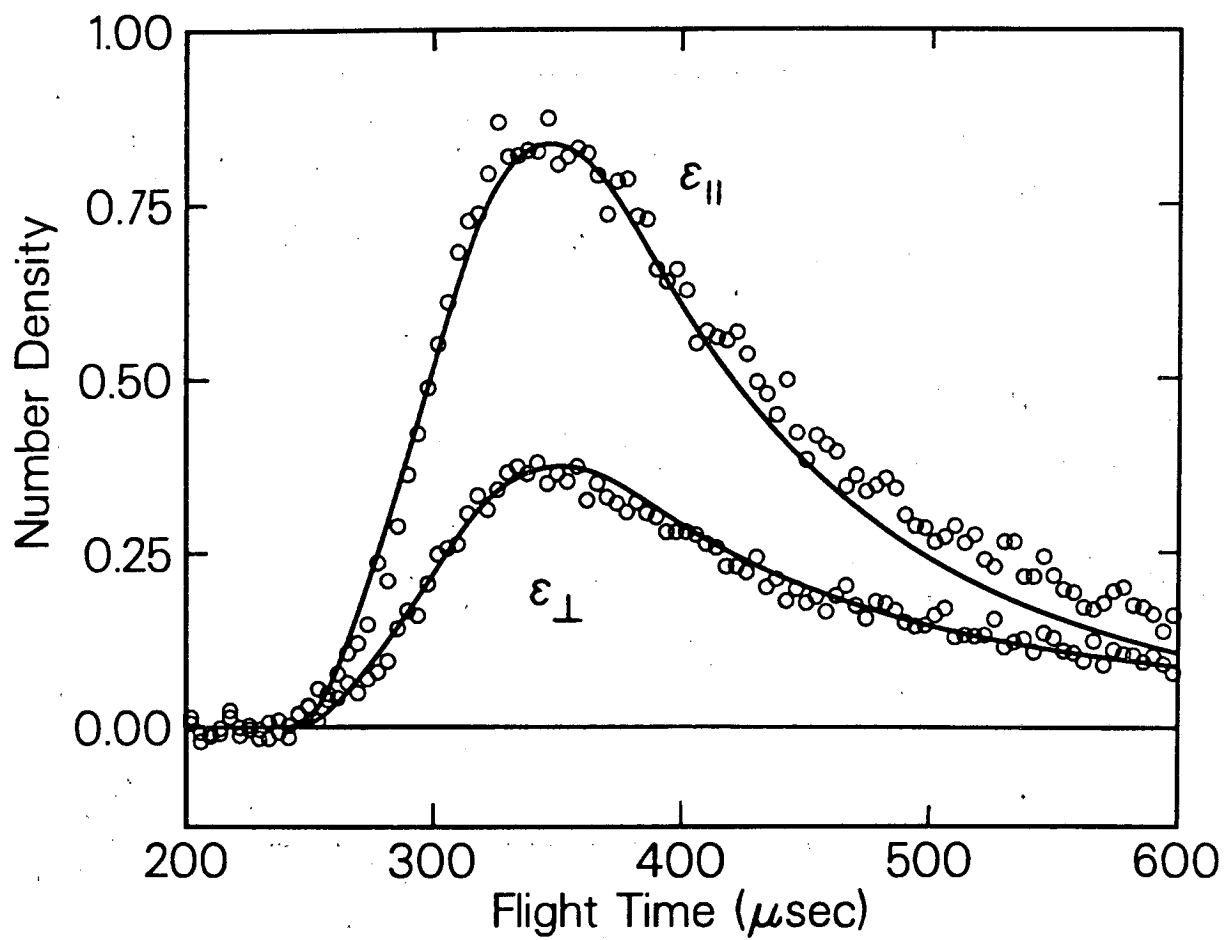
XBL 8811-3911

Fig. 6

XBL 8610-3673

Fig. 7

Fig. 8

XBL 8610-3672 A

XBL 8610-3670

Fig. 9

Fig. 10

XBL 8610-3671